

# Transformation of Fenuron Induced by Photochemical Excitation of Humic Acids

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**Abstract:** When neutral solutions containing the herbicide 3-phenyl-1,1-dimethylurea (fenuron) and a humic acid are irradiated at 365 nm, 3-(4-hydroxyphenyl)-1,1-dimethylurea and three biphenyl products are formed as main products. The apparent quantum yield of fenuron disappearance is evaluated as  $6.2 \times 10^{-5}$  mole E<sup>-1</sup>.

Upon irradiation of the same mixture at 253.7 nm, both direct and induced phototransformations of fenuron occur. Direct photooxidation yields 2- and 4-amino-*N,N*-dimethylbenzamide. The induced phototransformation leads to 2- and 4-hydroxylation of the aromatic ring in accordance with the fact that hydroxyl radicals are involved in the oxidation.

**Key words:** fenuron, humic acid, photoinduced transformation, aqueous solution.

## 1 INTRODUCTION

Phenylurea herbicides are commonly used on agricultural sites.<sup>1</sup> As a consequence, these compounds are expected to be present in soil or in the aquatic environment in measurable amounts. Phototransformation is a possible abiotic degradation process. Among phenylurea herbicides, fenuron does not absorb light at wavelengths longer than 290 nm and is photostable under natural light. For such a compound, indirect phototransformation is an alternative degradation pathway. Humic acids which are naturally occurring substances were reported to produced active oxygen species upon irradiation.<sup>2–4</sup> They should thus be able to photoinduce the transformation of organic substances.

The present work is a study of the transformation of fenuron induced by excitation of a commercial humic acid. The reaction was studied at two excitation wavelengths (253.7 and 365 nm). It was compared to the direct phototransformation of fenuron at 253.7 nm and to the oxidation of fenuron photosensitized by acetophenone.

## 2 MATERIALS AND METHODS

Reactants were of the highest grade available and used as received. Humic acid was purchased from Aldrich. Water was purified with a Milli-Q device (Millipore).

Solutions of fenuron and humic acid (0.1 g litre<sup>-1</sup>) were prepared by dissolving reactants in Milli-Q water and the pH was adjusted to 6.5 with phosphate buffer (0.002 M). The humic acid is completely soluble at the concentration used. The solutions were filtered on Millipore 0.45 µm before irradiation.

Solutions were irradiated at 253.7 nm in a cylindrical quartz cell located on the axis of a cylindrical mirror equipped with six monochromatic low-pressure mercury lamps (germicide lamps TUV, Philips) and at 365 nm in a water-cooled reactor using three 'black light' lamps (HPW 125 W, Philips). 90% of the energy was emitted at 365 nm, 5% at 334 nm and a few percent at 391 and 405 nm. Photon flows were evaluated from chemical actinometers in conditions of total absorption. Under the conditions used,  $2.0 \times 10^{-5}$  E l<sup>-1</sup> s<sup>-1</sup> entered the sample at 253.7 nm and  $5.4 \times 10^{-5}$  E l<sup>-1</sup> s<sup>-1</sup> at 365 nm. For irradiations at 313 nm, a monochromator (Bausch and Lomb)

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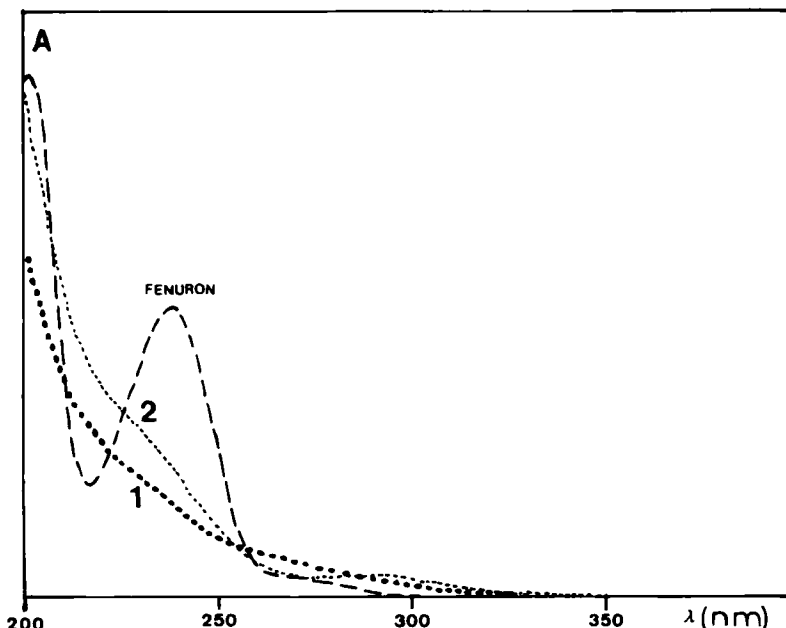


Fig. 1. UV spectra of fenuron, 1 and 2 in methanol + water (30 + 70 by volume).

equipped with a high-pressure mercury arc (200 W) was used.

UV spectra were recorded on a Cary 118C and fluorescence spectra on a Perkin Elmer MPF 3L. High performance liquid chromatography (HPLC) was carried out in deuteromethanol on a Waters chromatograph equipped with a photodiode array detector (model 990) and a  $C_{18}$  Lichrosphere column ( $5\ \mu\text{m}$ ,  $250 \times 4\ \text{mm}^2$ ). Water + acetonitrile (80 + 20 by volume) was used for the separation of the reaction products. Isolation of photoproducts was performed with a preparative HPLC Gilson equipped with a  $C_{18}$  Microsorb column ( $3\ \mu\text{m}$ ,  $100 \times 24\ \text{mm}^2$ ).

### 3 RESULTS

#### 3.1 Direct phototransformation at 253.7 nm

The molar extinction coefficient of fenuron at 254 nm is  $3200\ \text{M}^{-1}\ \text{cm}^{-1}$ . Irradiation of a neutral aqueous solution of fenuron ( $2 \times 10^{-4}\ \text{M}$ ) yielded two photoproducts, formation of which was not influenced by the presence of oxygen. These products were separated by HPLC and analysed by NMR and mass spectrometry. The following data were obtained:

1: mass spectrum  $m/e$  164; [ $^1\text{H}$ ] NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  7.55 (d, 2H,  $J = 8.2\ \text{Hz}$ ), 7.20 (d, 2H,  $J = 8.2\ \text{Hz}$ ), 3.25 (s, 6H)

2: mass spectrum  $m/e$  164; [ $^1\text{H}$ ] NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  7.40 (t, 1H,  $J = 7.9\ \text{Hz}$ ), 7.30 (d, 1H,  $J = 7.9\ \text{Hz}$ ), 7.01 (d, 1H,  $J = 7.9\ \text{Hz}$ ), 6.93 (t, 1H,  $J = 7.9\ \text{Hz}$ ), 3.25 (s, 6H)

UV spectra are given in Fig. 1. These products were identified as, respectively, 4- and 2-amino-*N,N*-dimethylbenzamide.

A conversion of 14% was obtained in samples irradiated for 5 min. The quantum yield of fenuron disappearance,  $\phi_d$ , defined as  $\Delta(\text{fenuron})/\Delta t \cdot I_a^f$  where  $I_a^f$  is the light intensity absorbed by fenuron, was evaluated as  $6.0 \times 10^{-3}\ \text{mole E}^{-1}$  in absence or in the presence of oxygen.

#### 3.2 Irradiation at 253.7 nm of mixtures of fenuron and humic acid

Upon irradiation of a neutral solution containing fenuron ( $2 \times 10^{-4}\ \text{M}$ ) and the humic acid ( $0.1\ \text{g litre}^{-1}$ ), two further products were formed along with 1 and 2 (Fig. 2):

3: mass spectrum  $m/e$  180; [ $^1\text{H}$ ] NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  7.30 (d, 2H,  $J = 8.8\ \text{Hz}$ ), 6.89 (d, 2H,  $J = 8.7\ \text{Hz}$ ), 3.19 (s, 6H)

4: mass spectrum  $m/e$  180; [ $^1\text{H}$ ] NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  7.67 (dd, 1H,  $J = 7.9\ \text{Hz}$ ,  $J = 1.5\ \text{Hz}$ ), 7.11 (td, 1H,  $J = 7.9\ \text{Hz}$ ,  $J = 1.7\ \text{Hz}$ ), 7.02 (dd, 1H,  $J = 8\ \text{Hz}$ )

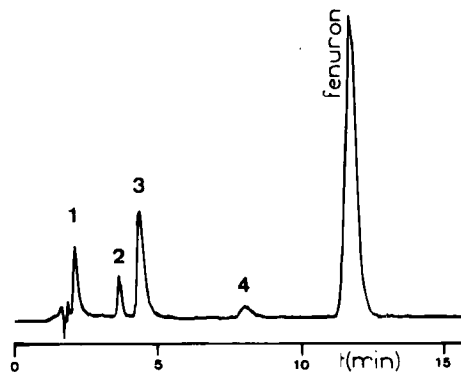


Fig. 2. HPLC chromatogram of a neutral solution containing fenuron ( $2 \times 10^{-4}\ \text{M}$ ) and humic acid ( $0.1\ \text{g litre}^{-1}$ ) irradiated at 253.7 nm.

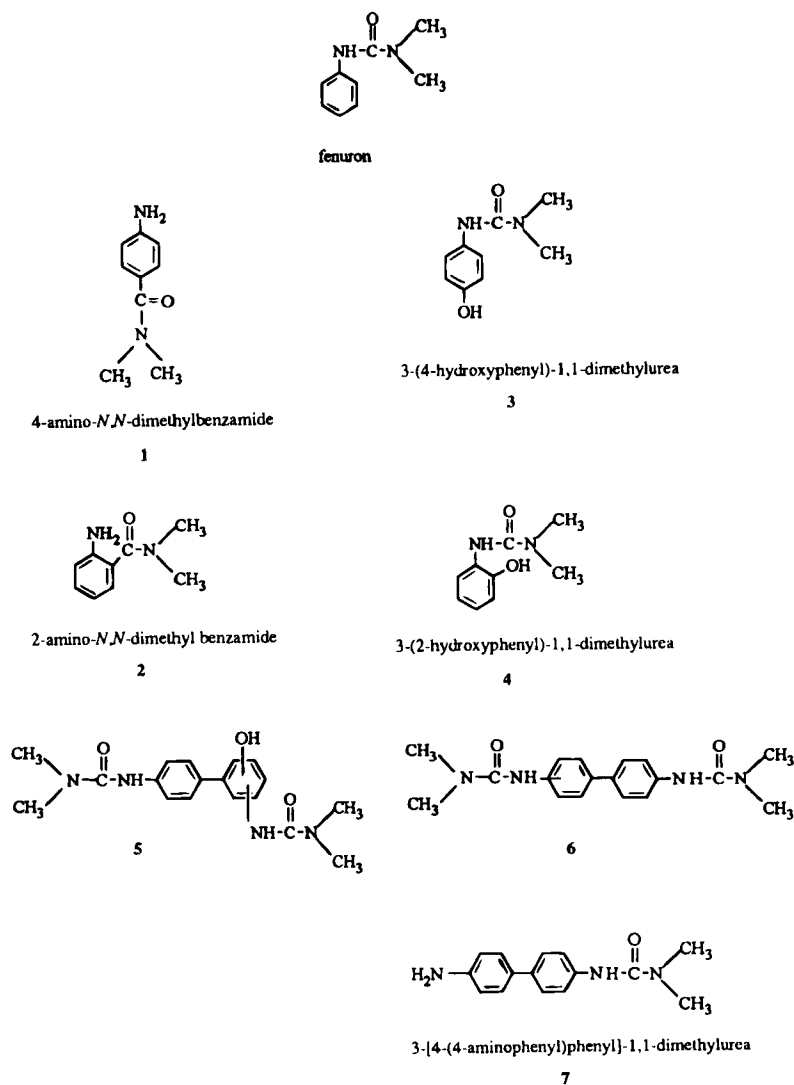
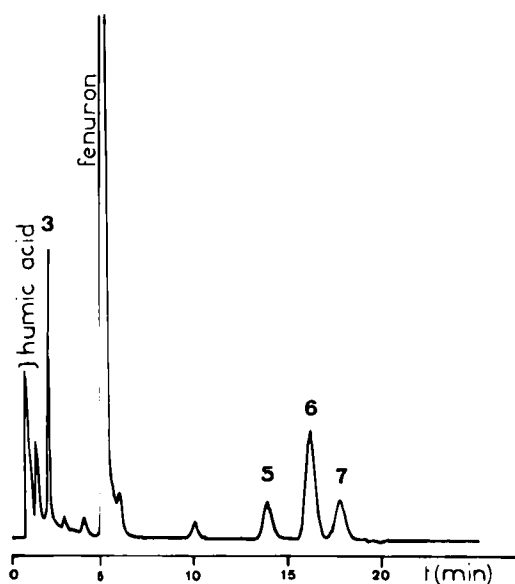
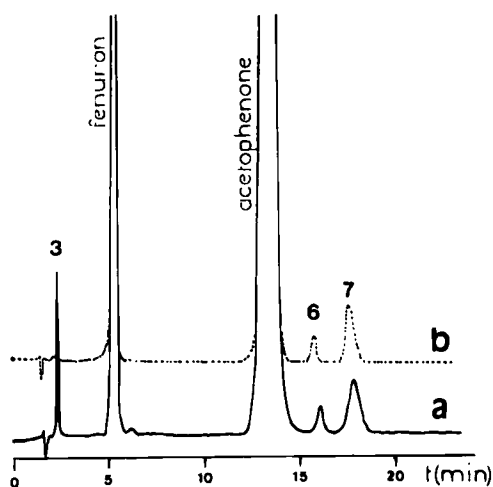


Fig. 3. Structures of compounds discussed.

Fig. 4. HPLC chromatogram of a neutral solution containing fenuron ( $10^{-3}$  M) and humic acid ( $0.1 \text{ g litre}^{-1}$ ) irradiated at 365 nm.Fig. 5. HPLC chromatogram of neutral solutions containing fenuron ( $10^{-3}$  M) and acetophenone ( $4 \times 10^{-4}$  M) irradiated at 313 nm; (a) oxygen-saturated solution; (b) argon-saturated solution.

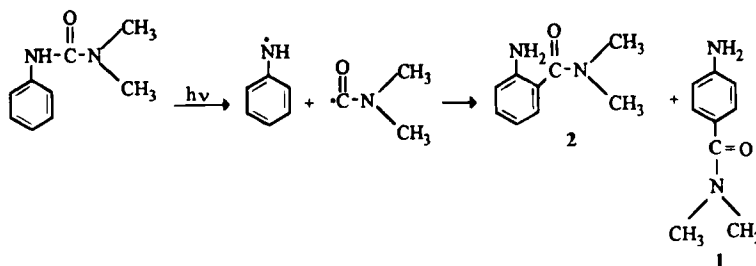


Fig. 6. Formation of compounds 1 and 2 from fenuron.

$J = 1.5$  Hz); 6.97 (td, 1H,  $J = 7.8$  Hz,  $J = 1.5$  Hz), 3.25 (s, 6H)

3 and 4 can be assigned to the 4- and 2-hydroxylated derivatives (Fig. 3). When an hydroxyl radical scavenger like isopropanol was added to the solution, the formation of 4 was completely inhibited and that of 3 only partly reduced (2/3). It can be concluded that 4 is produced exclusively in the oxidation of fenuron by hydroxyl radicals, whereas 3 is also formed by other pathways.

Addition of the humic acid ( $0.1 \text{ g litre}^{-1}$ ) to the solution of fenuron resulted in a decrease of the rate of fenuron disappearance. In this mixture, photons can be absorbed by both fenuron and the humic acid. The apparent quantum yield of fenuron transformation  $\phi_a$  can be written:

$$\phi_a = \frac{\Delta(\text{fenuron})}{I_a \cdot t} = \phi_d \frac{I_a^f}{I_a} + \phi_i \frac{I_a^{\text{HA}}}{I_a}$$

where  $I_a^f$  and  $I_a^{\text{HA}}$  are light intensities absorbed respectively by fenuron and the humic acid in the mixture,  $I_a$  is the sum  $I_a^f + I_a^{\text{HA}}$  and  $\phi_i$  is the quantum yield of induced phototransformation. In the present experimental conditions,  $\phi_a$  is  $1.7 \times 10^{-3}$ . From the values of the absorbances  $\text{OD}^f = 0.64$  and  $\text{OD}^{\text{HA}} = 3.5$ , the ratios  $I_a^f/I_a$  and  $I_a^{\text{HA}}/I_a$  can be calculated by the relationships:

$$I_a^f/I_a = \frac{\text{OD}^f}{\text{OD}^f + \text{OD}^{\text{HA}}}$$

and

$$I_a^{\text{HA}}/I_a = \frac{\text{OD}^{\text{HA}}}{\text{OD}^f + \text{OD}^{\text{HA}}}$$

and  $\phi_i$  is evaluated as about  $1.0 \times 10^{-3} \text{ mole E}^{-1}$ .

### 3.3 Irradiation at 365 nm of mixtures of fenuron and humic acid

At this wavelength, fenuron does not absorb photons and the absorbance of a  $0.1 \text{ g litre}^{-1}$  aqueous solution of humic acid is 1. Figure 4 gives a typical HPLC chromatogram obtained upon irradiation at 365 nm of a neutral solution containing fenuron ( $10^{-3} \text{ M}$ ) and the humic acid ( $0.1 \text{ g litre}^{-1}$ ) after 20% conversion of fenuron. Four main photoproducts were obtained: 3, 5,

6 and 7. Formation of 1, 2 and 4 was not observed; 5 and 6 were isolated together. Data on mass spectra were in agreement with biphenyl structures:  $m/e$  342 and 327 (Fig. 3). 7 was separated independently and analysed, giving the following data: mass spectrum  $m/e$  255;  $^1\text{H}$  NMR  $\delta$  7.69 (d, 2H,  $J = 9$  Hz), 7.60 (d, 2H,  $J = 9$  Hz), 3.25 (s, 6H); UV  $\lambda_{\text{max}}$  287 nm. 7 was highly fluorescent with a maximum emission at 342 nm. From these results, 7 was identified as 3-[4-(4-aminophenyl)phenyl]-1,1-dimethylurea (Fig. 3).

Isopropanol had no influence on the reaction, indicating that hydroxyl radicals were not involved. Relative proportions of biphenyls increased with increasing fenuron concentration.

The apparent quantum yield of fenuron disappearance was evaluated as  $6.2 \times 10^{-5}$  for an initial fenuron concentration equal to  $10^{-3} \text{ M}$ .

### 3.4 Irradiation at 313 nm of mixtures of fenuron and acetophenone

Irradiation at 313 nm of oxygen-saturated neutral solutions containing fenuron ( $10^{-3} \text{ M}$ ) and acetophenone ( $4 \times 10^{-4} \text{ M}$ ) led to the formation of 3, 6 and 7. In deoxygenated solutions, formation of product 3 was not observed (Fig. 5).

## 4 DISCUSSION

Formation of 1 and 2 upon photolysis of fenuron at 254 nm can be explained by the cleavage of the

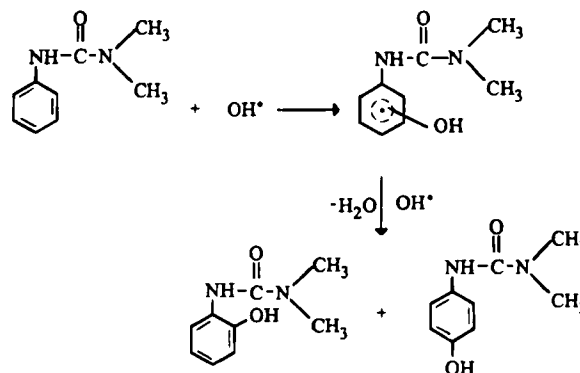


Fig. 7. Oxidation of fenuron by hydroxyl radicals formed by excitation of humic acid at 253.7 nm.

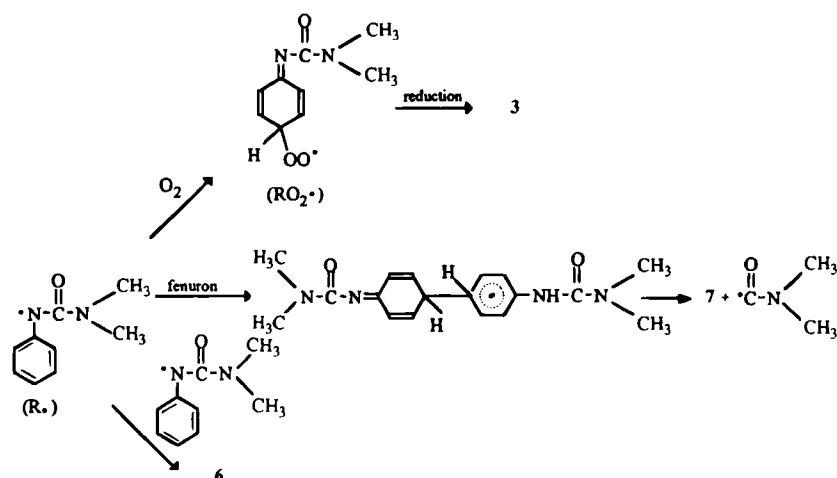


Fig. 8. Reaction of fenuron in presence of acetophenone at 313 nm.

nitrogen-carbon bond, followed by the recombination of the radical pair, as shown in Fig. 6. Such a reaction has been observed in the photolysis of fenuron in alcoholic solution.<sup>5</sup>

Oxidation of fenuron by hydroxyl radicals formed by excitation of the humic acid at 253.7 nm leads to hydroxylation in the 2- and 4-positions of the aromatic ring according to the mechanism shown in Fig. 7.

Product 3 and biphenyls are the main products observed upon irradiation at 365 nm of a neutral solution containing fenuron and the humic acid. Products obtained at 313 nm with acetophenone as photosensitizer are the same, even though product distribution is somewhat different. Since fenuron does not absorb photons at these wavelengths, only photoinduced transformations occur. Excited acetophenone is expected to abstract a hydrogen atom from fenuron<sup>6</sup> leading to a free radical ( $R^\bullet$ ) which can react in several ways, as shown in Fig. 8.

In argon-saturated solutions, 3 is not produced. This observation confirms that oxygen is required in the formation of this product. It is interesting to observe that oxidation by hydroxyl radicals leads to hydroxylation in the 2- and 4-positions, whereas oxidation induced by excitation of humic acids or acetophenone occurs only at the 4-position. In the photocatalytic transformation of phenolic derivatives, similar phenomena have been observed.<sup>7</sup>

Irradiation of the humic acid produces excited chromophores or free radicals able to abstract a hydrogen atom from fenuron, leading to  $R^\bullet$ . This free radical reacts by the processes mentioned above.

The relative amounts of 6 and 7 are five times lower with humic acid than with acetophenone, indicating that the complex structure of the humic acid plays a role in the fate of  $R^\bullet$ .

In conclusion, humic acids are able to photoinduce the transformation of fenuron. At 254 nm, hydroxyl radicals are photoproduced, leading to products hydroxylated in the 2- and 4-positions. At this wavelength, direct photolysis of fenuron also occurs yielding 2- and 4-amino-*N,N*-dimethylbenzamide. At 365 nm, 4-hydroxylated fenuron and biphenyls are formed by excitation of the humic acids. Results obtained with acetophenone as photosensitizer are qualitatively similar, showing that both reactions have the same intermediate (i.e.  $R^\bullet$ ).

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